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(54) Title: PLATINUM-FREE CHELATE-CATALYST MATERIAL FOR THE SELECTIVE  
REDUCTION OF OXYGEN AND METHOD FOR THE PRODUCTION THEREOF

(55) Abstract: Platinum-free chelate-catalyst materials for the selective reduction of oxygen have application in hydrogen and methanol fuel cells. Conventional catalyst material comprises an unsupported transition metal and a nitrogen- and a carbon-donor, which are polymerized to give a carbon matrix under pyrolytic conditions, in which the unsupported transition metal, functioning as electron donor and a nitrogen-coordinated transition metal chelate are bonded. The achievable porosity, catalytic activity and stability are however not adequate for commercial applications. Said chelate catalyst material comprises, in addition to the at least one unsupported transition metal, a nitrogen-containing organometallic transition complex, with a further transition metal different to the said transition metal and a chalcogenic component. The advantages of various transition metals and the chalcogens as electrically conducting bridge formers can thus be combined. The unsupported transition metal in the form of a salt serves as filler during the formation of the carbon matrix, such that the above is embodied as an ultra-highly-porous material due to a foaming effect on the thermal decomposition of said salt. Said chelate-catalyst material is particularly suitable for application in commercial industry, for example the auto-industry as a result of the high activity, stability and low cost thereof.

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## **Platinum-free chelate-catalyst for the selective reduction of oxygen and method for the production thereof.**

### **<<5>> Description**

The invention relates to a platinum-free chelate-catalyst material for the selective reduction of oxygen, containing at least one unsupported transition metal, one nitrogen component and one carbon component in the form of a porous conductive carbon matrix, <<10>> into which the unsupported transition metal functioning as electron donor and a nitrogen-coordinated transition metal chelate functioning as catalysis centre are bound, and to a method for the production thereof.

<<15>> A central field of application of catalysts are electrochemical cells, in particular emission-free fuel cells, which generate electrical power in an efficient and environmentally friendly manner by converting the chemical energy of a fuel-oxidation reaction into electrical energy, without an intermediate thermal energy stage. <<20>> Fuel cells are most efficient when hydrogen is converted to electrical energy *<sic>*. Notable among the many types of fuel cells is the polymer-electrolyte-membrane (PEM) fuel cell, which is very suitable for an operation with hydrogen / oxygen or hydrogen / air. But the low energy density of hydrogen creates a problem, which is the reason why increasingly methanol is used as fuel for mobile applications. <<25>> Methanol can either be broken down catalytically into hydrogen and carbon dioxide on board the vehicle (indirect methanol fuel cell) or can be oxidized directly at the anode. The direct methanol / air fuel cell (DMFC) is technically easier to realize <<30>> and for this reason can be considered a very promising electrochemical energy source for small devices and electric motors.

Up to now, preferred catalyst materials for the anode in DMFCs were mixed platinum / ruthenium sponges or so-called "carrier catalysts", in which superfine metal particles are deposited on a conductive support material such as carbon black or graphite. Pure platinum or supported platinum is used as cathode catalyst. <<5>> But pure platinum does not act very selectively as a catalyst which gives rise to problems when methanol is used as fuel. The cathode and the anode are separated by a proton-conducting membrane as a linkage between the anode and cathode, but this membrane is permeable to methanol, which can reach the cathode where it is oxidized. <<10>> As a result, the cathode, which is to serve for the reduction of air oxygen, is depolarized, which leads to output reductions.

The present invention relates to the field of platinum-free catalyst materials that selectively reduce oxygen and thus are alkanol-stable, in particular the group of chelate-catalyst materials. <<15>> A chelate is a very catalytically active higher-order complex compound, in which a central metal ion - making several bonds - is surrounded by a ring of one or several molecules or ions. Scientific literature already describes various platinum-free methanol-stable chelate-catalyst materials in supported and unsupported form. <<20>> But so far none of the known types of catalyst materials that are described in the following have been used in technical applications, since their catalytic activity and stability have been judged inadequate. The presence of highly conductive carbon with a large specific surface area is essential for technical applications. <<25>> During the high-temperature reactions of chelate, this does not only result in improved activity but also increases the stability of the catalyst material. In this regard one must distinguish between a direct introduction of conductive carbon, for example in the form of carbon black, <<30>> and an in situ production of the carbon matrix by polymerization of suitable organometallic chelates, which is what this invention relates to.

In regard to the in situ production of the carbon matrix, the review article [I] "Direct methanol – air fuel cells for road transportation", (B.D. McNicol et al., Journal of Power Sources 83 (1999) p. 15-13) discloses catalyst materials with non-noble metals for application in DFMCs <sic> (chapter 4.5.2). <<5>> Also described are alternatives for the preparation of organometallic chelate, such as iron porphyrin or cobalt porphyrin, phthalocyanine, as well as tetra-azo<sup>1</sup>-annulene. As an example, in the case of a metal tetraphenyl-porphyrin as active chelate, a metal ion is surrounded by four nitrogen ions (MeN<sub>4</sub>), each of which is part of a mono-pyrrole ring. <<10>> The catalytic activity of these compounds for the reduction of oxygen has also been known for some time. The results vary in dependence on the particular transition metals used in the chelates. For example, the use of cobalt results in a definite increase of the activity, while the use of iron produces a distinct increase in stability. <<15>> Even though there have been reports of excellent catalytic activity for some of these materials, the materials do not yet possess sufficient stability to be used in fuel cells.

<<20>> The publication [II] by Contamin et al. describes the preparation of a cobalt-containing fuel-cell catalyst by pyrolysis of cobalt-tetra-aza-annulene in the presence of active charcoal black (see O. Contamin, C. Debiemme-Chouvy, M. Savy, and G. Scarbeck: "Oxygen electroreduction catalysis: effect of sulfur addition on cobalt tetraazaannulene precursors", Electrochimica Acta 45 (1999), pp. 721-729). <<25>> The authors observed a clear increase of the catalyst activity after the addition of thiourea to the formulation of the preparation. The active centre consists of two opposing cobalt atoms, which are bound to the carbon skeleton via C-S bridges.

<<30>>

For the catalyst material described in **JP 59138066**, the preparation takes place by mixing transition metal compounds with cobalt, copper, nickel, molybdenum,

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<sup>1</sup> Should this be '-aza-'? (The Translator)

and/or tin with iron, urea, and for example a pyromellitic acid<sup>2</sup> anhydride with a subsequent temperature treatment in the presence of a conductive carbon substrate. This results in the formation of a metal-phthalocyanine polymer by means of an integration of the various employed transition metals, <<5>> which are bound as nuclei into the metal chelates. This material is suggested for application in alkaline fuel cells. As far as the parallel use of several different transition metals is concerned, another scientific publication must be mentioned, which reports on the catalytic activity of unsupported mixtures of cobalt tetra-phenyl-porphyrin (CoTPP) and iron tetra-phenyl-porphyrin (FeTPP). <<10>> According to the publication [III] by R. Jiang and D. Chu ("Remarkably Active Catalysts for the Electroreduction of O<sub>2</sub> to H<sub>2</sub>O for Use in an Acidic Electrolyte Containing Concentrated Methanol", Journal of the Electrochemical Society 147 (12), pp. 4605-4609 (2000), <<15>> electrochemical measurements of the binary mixture of CoTPP and FeTPP treated under argon at 600°C show an increased catalytic activity in comparison to the pure, temperature-treated substances. Still, the structure of the material is relatively compact and does not show a high degree of porosity.

<<20>>

The printed patent specification US 6 245 707 describes methanol-stable fuel-cell catalysts on nitrogen-chelate basis with at least two different transition metals (e.g. metal tetra-phenyl-porphyrin) for the reduction of oxygen, whereby a thermal treatment in the presence of a carbon substrate is used to convert the transition metals to an active cathode catalyst to be used in low-temperature fuel cells. <<25>>

The article [IV] "Oxygen reduction catalysts for polymer electrolyte fuel cells from the pyrolysis of Fe<sup>3+</sup> acetate adsorbed on 3,4,9,10-perylene tetra carboxylic dianhydride" by G. Faubert et al. (Electrochimica Acta 44 (1999) pp. 2589-2603) describes the preparation of a chelate-catalyst material by way of mixing an iron salt (acetate of iron) with perylene tetra carboxy anhydride (PTCDA) with a subsequent temperature treatment in ammonia (NH<sub>3</sub>) gas.

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<sup>2</sup> This term represents 'Pyromellithsäure'. I could not find a translation of the German 'Pyromellitinsäure' (The Translator)

A porous conductive carbon matrix is generated by the PTCDA and nitrogen is introduced by the  $\text{NH}_3$ . The introduction of this article points out that a transition metal originating from a salt, such as Fe or Co, as well as a nitrogen source and a carbon source, <<5>> are required for the production of a stable active metal-based catalyst material. This may in particular be realized in situ by a polymerization of the carbon source.

<<10>> The **background art** that the invention takes as a starting point is described in the article [V] "O<sub>2</sub> Reduction in PEM Fuel Cells: Activity and Active Site Structural Information for Catalysts Obtained by Pyrolysis at High Temperature of Fe Precursors" by M. Lefèvre et al. (J. Phys. Chem. B (2000)). Fe<sup>III</sup> acetate as a precursor compound is mixed with PTCDA as the organic compound in the presence of  $\text{NH}_3$  as nitrogen precursor compound and is subjected to pyrolysis at high temperatures above 800°C. <<15>> Polymerization of the metal-free and nitrogen-free PTCDA in situ generates a porous conductive carbon matrix, into which individual iron atoms functioning as electron donors and iron chelate, coordinated by four nitrogen atoms, are adsorptively bound. <<20>> It can be learned from the article that the iron content and the pyrolysis temperature can be used to influence the catalytic activity of the chelate-catalyst material. But due to the comparatively low porosity that is obtained, this activity is not yet adequate for commercial applications. Moreover, adequate stability has not yet been obtained. <<25>> Furthermore, a matrix former and a separate nitrogen donor are required during the synthesis in addition to the transition metal salt.

Consequently, the **objective** of the present invention is to specify a platinum-free chelate-catalyst material of the above-mentioned class <<30>> that possesses especially high catalytic activity and stability so that it is especially suitable for commercial applications.

As part of this, the knowledge of the effects of various transition metals and the achievable porosity gained from the background art is to be taken into consideration. In addition, the chelate-catalyst material according to the invention is to possess as few components as possible and also should be simple to produce on an industrial scale in only few manufacturing steps. <<5>>

For this reason, to provide a **solution** to this problem, the invention intends in regard to its chelate-catalyst material with at least one unsupported transition metal and one nitrogen component and one carbon component, <<10>> that the nitrogen component and the carbon component are realized as a joint nitrogen-containing organometallic transition complex with a further transition metal – different from the unsupported transition metal –, whereby the further transition metal is nitrogen-coordinated with regard to the transition metal chelate, and further intends that an organic chalcogen compound is also bound into the carbon matrix as an electron-conducting bridge former <<15>> between the unsupported transition metal, which is only present in an isolated form in the carbon matrix, and the coordinated transition metal chelate.

<<20>> In the chelate-catalyst material according to the invention, polymerization is used to form a carbon skeleton with structures down to the nanometer scale from the nitrogen-containing organometallic transition complex. Due to bound ions of the at least two transition metals, the carbon skeleton is both electrically conductive and interspersed with catalytic reaction centres. <<25>> The bound ions of the unsupported transition metal primarily act as electron donors for the reaction centres, which consist of the further transition metal in the nitrogen-containing organometallic transition complex and are coordinated by nitrogen atoms with respect to active Me-N<sub>4</sub> nuclei. <<30>> The combination of different transition metals in the chelate-catalyst material according to the invention makes it possible to combine the advantageous characteristics of the transition metals additively for use in various functions. Suitable choices of



the transition metals, one group of which is bound into the carbon matrix as electron donors while the other group serve as chelate nuclei, can significantly increase the catalytic activity on the one hand, and the stability on the other hand. <<5>> The further chalcogen component in the chelate-catalyst material according to the invention contributes to a further increase of the catalytic activity. The unsupported transition metal and the coordinated transition metal are connected electrically conductively by integrated chalcogen bridges, which enables an especially good electron transfer from the electron-donating transition metal to the catalytically active transition metal in the chelate nuclei. <<10>>

In the chelate-catalyst material according to the invention, only a small portion of the unsupported transition metal, which is created during the synthesis of the used precursor compound, is bound into the carbon matrix. <<15>> The by far largest portion serves as filler that forms nano pores during the in-situ generation of the carbon matrix, and is washed out in a separate processing step after the pores have been formed (see below). In this regard, the catalyst material according to the invention is different from the above-described fuel-cell catalysts. <<20>> The additional space-reserving function of the unsupported transition metal results in a highly porous structure of the carbon matrix, which also contributes to increasing the catalytic activity by enlarging the active surface area. Thus, the unsupported transition metal, added for example in the form of a metal oxalate, acts as a foaming agent during the polymerization of the nitrogen-containing transition metal chelate. <<25>> Moreover, the chelate-catalyst material according to the invention is made up of only a small number of components, since the nitrogen donor and the carbon donor are combined in a single material component. <<30>>

The platinum-free chelate-catalyst material described by the invention may be used in the cathode of a fuel cell. The costs of this material are at most one tenth of the costs of a

platinum-containing catalyst material. Thus, application of the material according to the invention would contribute to a significant reduction of the costs of a fuel cell module of conventional design, which still uses platinum-containing catalyst materials. <<5>> As additional advantages of the chelate-catalyst material according to the invention one has to mention the unlimited availability of the components that are used and the alkanol stability, as a result of which leaking of methanol to the cathode would not result in a drop in performance of the fuel cell.

<<10>>

Other improvements arise from the further developments of the invention's chelate-catalyst material in accordance with the dependent claims. In particular, one of these improvements may be that at least one of the unsupported transition metals is a group VIII transition metal, in particular iron or ruthenium. <<15>> The elements of this group possess a particularly high catalytic activity and they are often used in the form of finely distributed particles. Not only does the presence of these particles cause the reacting substance to physically attach to the surface (adsorption), it also causes a chemical activation of the adsorbed particles. <<20>> In particular ruthenium possesses activity that is comparable to that of platinum but it is not as expensive as platinum. It presents a promising alternative to platinum. It is true that the raw-material costs for ruthenium as a noble metal are higher than those of simple transition metals and that ruthenium has a lower specific catalytic activity. But a suitable processing can significantly increase its catalytic activity. <<25>> Also possible is a combination of different transition metals, whereby the effects may be increased by ion formation or by forming nano particles from the chosen transition metals. In particular, if ruthenium is used as the unsupported transition metal, it can form especially small nano particles, <<30>> which then lead to a carbon matrix with ultra-high porosity. In addition, ruthenium is a good electron donor. Its use results in an increase of both catalytic activity and stability.

If the at least one further transition metal – different from the unsupported transition metal – in the nitrogen-containing organometallic transition complex is a group VIII transition metal, <<5>> then, according to a further development of the invention, it may be cobalt or iron. Combining iron as unsupported transition metal and cobalt as transition metal in the nitrogen-containing organometallic transition complex makes it possible to use the advantages of both for the catalysis in an optimum manner. <<10>> Iron is an excellent electron donor and its positive effect on the catalysis has already been described above. In addition, iron increases stability, while cobalt increases the activity of the catalyst material. Advantageously, a metalloporphyrin may be used as the nitrogen-containing organometallic transition complex. The metalloporphyrin may contain cobalt or iron and in particular may be realized as cobalt tetra-methoxy-phenyl-porphyrin or iron tetra-methoxy-phenyl-porphyrin. Metalloporphyrin possess excellent catalytic characteristics because the active transition metals are coordinated freely in space by four nitrogen bonds. <<20>> This results in an optimum surface area accessibility and catalytic effect. Combining this with the other transition metal as unsupported transition metal increases these effects even more. Both or several transition metals may be used in the metalloporphyrin for this purpose. The nitrogen donor and the carbon donor are combined in the metalloporphyrin. <<25>> The metalloporphyrin polymerizes in highly cross-linked structures already at moderate processing temperatures in the region of 450°C and during the synthesis in-situ forms a carbon matrix that possesses ultra-high porosity but is still stable. The in situ production causes an especially homogeneous distribution of the electron donors and the active nuclei in the carbon matrix, <<30>> which ensures a uniformly high quality of the chelate-catalyst material according to the invention. But it is also possible to include a carbon carrier,

in particular in the form of carbon black, to support the formation of the carbon matrix. For example, an electron-donating transition metal may be carbon-supported and in this manner simplify and improve the adsorptive incorporation into the carbon matrix during manufacturing<sup>3</sup>. <<5>>

The positive effects of transition metals on the electrochemical catalysis are well known. But the organic chalcogen compound, which is additionally used in the chelate-catalyst material according to the invention, also has a significant effect on the catalytic activity, <<10>> in particular in the form of a catalytic initiating effect. In this regard, it may be additionally intended in an advantageous manner that the chalcogen is added in elementary form (e.g. sulphur) or in the form of an organic chalcogen compound (e.g. thiourea). The positive effects of sulphur, in particular as bridge former, are well known, as are its lower toxicity compared to selenium and its plentiful availability. For this reason, a further development of the invention may be the use of thiourea as the organic chalcogen compound, since thiourea is easy to synthesize and can be used in many ways. Urea ( $\text{OC}(\text{NH}_2)_2$ ) or carbamide also contains nitrogen. Thus, this offers the additional benefit that in the catalyst material according to the invention an additional nitrogen donor is available for the coordination during the chelate formation.

An especially simple and favourable method to manufacture a platinum-free chelate-catalyst material for the selective reduction of oxygen <<25>> with at least one unsupported transition metal, one nitrogen component and one carbon component in the form of a porous conductive carbon matrix, into which the unsupported transition metal is bound as electron donor and a nitrogen-coordinated transition metal chelate is bound as catalysis centre, <<30>> includes the following processing steps:

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<sup>3</sup> The original German sentence contains a grammar mistake making the exact meaning unclear. This is the meaning making most sense. (The Translator)

- Mixing a transition metal salt as precursor compound for the unsupported transition metal with the nitrogen-containing organometallic transition complex and the organic chalcogen compound
- <<5>> Heating the mixture to a pyrolysis temperature in the region of 450°C over the period of a few hours
- Cooling the polymerized mixture and mixing it with an acid
- Boiling the acid mixture for a time period of several minutes and subsequent cooling
- <<10>> Siphoning off the resulting powder and washing with de-ionized water
- Drying the powdery chelate-catalyst material

During the production of the chelate-catalyst material according to the invention, at first a sponge-like, transition-metal-containing carbon skeleton is produced <<15>> by at first using a mixing process to coat a fine transition metal salt powder with the nitrogen-containing organometallic transition complex and the organic chalcogen compound. Subsequently the mixture is subjected to pyrolysis at a moderate temperature in the region of 450°C. <<20>> During this, the water of crystallization bound in the transition metal salt evaporates. Next, the organic chalcogen compound breaks down and the nitrogen-containing organometallic transition complex melts. The latter starts to polymerize, during which a strongly cross-linked and thus very stable carbon skeleton is formed. Simultaneously with this process, the at least one unsupported transition metal salt starts to break down. <<25>> During this, nano crystals are formed from the unsupported transition metal, accompanied by the generation of gas. But a portion of the transition metal is strongly bound to the carbon matrix. The carbon skeleton, which has been formed from the polymerized nitrogen-containing organometallic transition complex, settles down around the nano crystal of the at least one transition metal. <<30>> At the chosen moderate processing temperature, the

coordination sphere for the  $\text{MeN}_4$  nuclei is largely retained. The chalcogen from the organic chalcogen compound is bound into the carbon matrix as electrically conducting bridges between the unsupported transition metal and the chelate nuclei. <<5>> The formed nano crystals are then washed out in a subsequent step, which is completely novel for synthesis processes of this type, and the result is a conductive, highly porous carbon matrix that possesses nano structures and microstructures and contains transition metals, chalcogen, and nitrogen.

<<10>> The resulting highly porous carbon matrix already possesses excellent stability and activity for the selective reduction of oxygen. But this activity can be increased even further according to an especially favourable further development of the process, which entails an additional processing step, to be carried out before or after the processing step of boiling the acid mixture:

<<15>>

- Heating the powdery chelate-catalyst material in a protective atmosphere to a high temperature in the region of  $850^\circ\text{C}$  over a time period of one hour or longer.

<<20>> It also may be intended that iron oxalate is provided as precursor compound to provide iron as an unsupported transition metal. Oxalate is the salt of oxalic acid, is very reactive, and can be made available at low cost on a large scale.

<<25>>

In the following, the favourable mode of action of the chelate-catalyst material according to the invention will be explained in more detail with the help of an embodiment example and figures.

<<30>> **Fig. 1** shows a thermogravimetric decomposition curve of the unsupported metal (iron oxalate) in the presence of the platinum-free chelate-catalyst material.

**Fig. 2** shows a picture of the platinum-free chelate catalyst material after the end of the preparation taken by a scanning electron microscope.

**Fig. 3** shows an EXAFS spectrum in the presence of the platinum-free chelate-catalyst material.

**Fig. 4** shows a current-density plot of the platinum-free chelate-catalyst material with a standard platinum catalyst as comparison.

### Embodiment Example

3.35 g of iron oxalate  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  as precursor compound, 0.65 g cobalt tetramethoxy-phenyl-porphyrin (CoTMPP) as nitrogen-containing organometallic transition complex, and 0.18 g of thiourea as organic chalcogen compound are mixed and are heated to  $450^\circ\text{C}$  for two hours and subsequently to  $850^\circ\text{C}$  for one hour. The mixture is cooled and in an argon atmosphere is suspended with 300 ml 1N HCL solution, and subsequently is heated to boiling for 30 minutes. After the cooling, the black powder is sucked off on the filter arrangement and is washed with plenty of de-ionized water. Subsequently, the powder is dried.

In this embodiment example, a sponge-like iron-containing carbon skeleton is produced by coating a fine iron oxalate powder with CoTMPP and thiourea. This mixture of iron oxalate, CoTMPP, and thiourea is then subjected to a temperature treatment. During this, at first the water of crystallization bound in the iron oxalate evaporates. Then the thiourea breaks down. The CoTMPP melts and starts polymerizing, which results in the formation of a cross-linked carbon skeleton. Please see Fig. 1 in this regard, which shows a thermogravimetric curve (mass loss TG, plotted as line) of the two-stage decomposition of cobalt-tetra-methoxy-phenyl-porphyrin (CoTMPP) in the presence of iron oxalate. In a first stage, the water of crystallization of the iron oxalate is released, indicated by the simultaneously measured mass signal  $m/e = 18$  (dashed line in the upper graph). In a second stage, iron oxalate decomposes ( $m/e = 44$ , formation of  $\text{CO}_2$ , dotted curve in the

upper diagram), as well as CoTMPP in the same temperature interval, as revealed by the mass  $m/e = 78$  (formation of  $C_6H_6$ , dash-dotted line in the lower diagram).

<<5>> The decomposition of the iron oxalate commences during the polymerization process. During this, iron oxide (FeO) nano crystals are formed, whereby  $CO_2$  and CO gas is produced, but a portion of the iron is also strongly bound into the carbon structure. During this, the carbon skeleton being formed from the polymerizing CoTMPP attaches around these nano crystals. <<10>> The coordination sphere of the cobalt ions is largely preserved at the temperature at which these processes proceed. The sulphur that is released by the thiourea is integrated into the carbon matrix as electrically conducting bridge between the electron-donating iron and the catalytically active cobalt chelate. <<15>> The nitrogen atoms, which are also released during the decomposition, are used – in addition to the nitrogen atoms from the CoTMPP – in the coordination of the cobalt atoms with respect to the chelate nuclei. The formed FeO crystals are then washed out in a subsequent processing step, and the result is a conductive, highly porous carbon matrix that contains iron, cobalt, nitrogen, and sulphur. <<20>> This substrate already possesses excellent activity for the selective reduction of oxygen. But this activity can be increased even further by a temperature treatment at  $850^\circ C$ .

In order to be able to assess the porosity of the catalytic material, the specific capacity of the catalyst material according to the invention was determined in electrochemical experiments with nitrogen. <<25>> The capacities that were achieved ranged between 100 and 300 F/g. These values are of the same order of magnitude as those of commercial highly porous carbon black. Furthermore, investigations using the scanning electron microscope confirmed the high porosity of the material down to the nanometer scale. <<30>> Regarding this, please see **Fig. 2**, which shows a picture of the



catalyst material according to the invention after an acid treatment taken with a scanning electron microscope. The highly porous structure is very evident.

In catalyst research, the fact that transition elements have a catalytic effect is considered as firmly established, since no chemical conversions take place in their absence. <<5>> Neither is the existence of the electron and its necessary participation in chemical reactions an open question in science. The distance between the transition metals and the elements nitrogen, carbon, and oxygen in the catalyst material according to the invention can be measured by means of Extended X-Ray Absorption Fine Structure (EXAFS) analysis using synchrotron radiation. <<10>> Regarding this please see Fig. 3, which shows Fourier-transformed EXAFS spectra at the Fe and the Co edge of a carbon-supported Fe-Co catalyst, which has been produced by pyrolysis of CoTMPP in the presence of iron oxalate. In order to remove pure metal particles, the catalyst was etched with acid prior to the measurement. <<15>> The positions of the peaks that have been found indicate that in addition to metal-carbon (carbides) and metal-oxygen (oxides), the catalyst material also contains metal-nitrogen bonds (nitrides), which are considered to be the nuclei of former nitrogen-coordinated transition metal chelates that are now integrated into a carbon support that has been formed in situ. <<20>>

### Electrochemical Characterization

10 mg of the chelate-catalyst powder obtained in this manner are mixed with a mixture of 1 ml of an ethanolic 0.2% Nafion solution and 1ml of de-ionized water and are suspended in an ultrasonic bath for 30 minutes. <<25>> 5  $\mu$ l of this suspension are then pipetted onto a polished glassy carbon electrode with a diameter of 1 mm and are air-dried. The working electrode prepared in this manner is measured in an electrochemical measuring cell with a 3-electrode configuration, <<30>> with a mercury sulphate electrode as reference electrode and a platinum wire as counter electrode, in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution as electrolyte in an O<sub>2</sub> saturated solution.

**Fig. 4** shows the diffusion-corrected current densities as a function of the potential difference between the working electrode and the counter electrode, with a standard platinum catalyst (20% platinum on Vulcan XC72R by Etek incrop., upper characteristic curve) as a comparison.

<<5>>

The voltage differences with respect to the Etek catalyst are:

- 60 mV            at 0.2 mA/cm<sup>2</sup>
- 40 mV            at 2 mA/cm<sup>2</sup>
- 20 mV            at 10 mA/cm<sup>2</sup> <<10>>
- 0 mV             at 20 mA/cm<sup>2</sup>

The measured voltage differences decrease as the current density increases and overall can be classified as extremely low in comparison to the state of the art. <<15>> This is why the platinum-free chelate-catalyst material according to the invention shows almost the same catalytic activity as a conventional standard catalyst material that uses expensive platinum.

**Patent Claims**

1. Platinum-free chelate-catalyst material for the selective reduction of oxygen, <<5>> containing at least one unsupported transition metal, one nitrogen component and one carbon component in the form of a porous conductive carbon matrix, into which are bound the unsupported transition metal functioning as electron donor and a nitrogen-coordinated transition metal chelate functioning as catalysis centre,

<<10>> **characterized in that**

the nitrogen component and the carbon component are realized together as a nitrogen-containing organometallic transition complex with an additional transition metal – different from the unsupported transition metal –, whereby the additional transition metal is nitrogen-coordinated with respect to the transition metal chelate, <<15>> and further characterized in that an organic chalcogen compound is also incorporated into the carbon matrix as electron-conducting bridge former between the unsupported transition metal, which occurs in isolated form in the carbon matrix, and the coordinated transition metal chelate.

<<20>>

2. Platinum-free chelate-catalyst material according to claim 1, **characterized in that** the at least one unsupported transition metal is a group VIII transition metal, in particular iron or ruthenium.

<<25>>

3. Platinum-free chelate-catalyst material according to claim 1 or 2, **characterized in that** the additional transition metal in the nitrogen-containing organometallic transition complex, which is different from the at least one unsupported transition metal, is a group VIII transition metal, in particular cobalt or iron.

<<30>>

4. Platinum-free chelate-catalyst material according to one of claims 1 to 3,  
**characterized in that**  
the nitrogen-containing organometallic transition complex is a  
metalloporphyrin. <<5>>
5. Platinum-free catalyst material according to claim 4,  
**characterized in that**  
the metalloporphyrin contains cobalt or iron and in particular is realized as  
cobalt-tetra-methoxy-phenyl-porphyrin (CoTMPP) or iron-tetra-methoxy-  
phenyl-porphyrin (FeTMPP). <<10>>
6. Platinum-free chelate-catalyst material according to one of claims 1 to 5,  
**characterized in that**  
an additional carbon component, in particular in the form of carbon black, is  
included to support the formation of the carbon matrix. <<15>>
7. Platinum-free chelate-catalyst material according to one of claims 1 to 6,  
**characterized in that**  
the chalcogen in the organic chalcogen compound is sulphur. <<20>>
8. Platinum-free chelate-catalyst material according to claim 8,  
**characterized in that**  
the organic chalcogen compound is thiourea.
9. <<25>> Method for manufacturing a platinum-free chelate-catalyst material  
according to claims 1 to 8 for the selective reduction of oxygen, containing at  
least one unsupported transition metal, one nitrogen component and one  
carbon component in the form of a porous conductive carbon matrix, into  
which are incorporated the unsupported transition metal as electron donor and  
a nitrogen-coordinated transition metal chelate as catalysis centre, <<30>>  
with the following processing steps:

- Mixing a transition metal salt as precursor compound for the unsupported transition metal with the nitrogen-containing organometallic transition complex and the organic chalcogen compound
  - <<5>> Heating the mixture to a pyrolysis temperature in the region of 450°C over the period of a few hours
  - Cooling the polymerized mixture and mixing it with an acid
  - Boiling the acid mixture for a time period of several minutes and subsequent cooling
  - <<10>> Siphoning off the resulting powder and washing with de-ionized water
  - Drying the powdery chelate-catalyst material
10. Method for manufacturing a platinum-free chelate-catalyst material according to claim 9, <<15>> with a further processing step, to be carried out before or after the processing step of boiling the acid mixture:
- Heating the powdery chelate-catalyst material in a protective atmosphere to a high temperature in the region of 850°C over a time period of one hour or longer.
- <<20>>
11. Method for manufacturing a platinum-free chelate-catalyst material according to claim 9 or 10, with iron oxalate as precursor compound to make iron available as the unsupported transition metal.

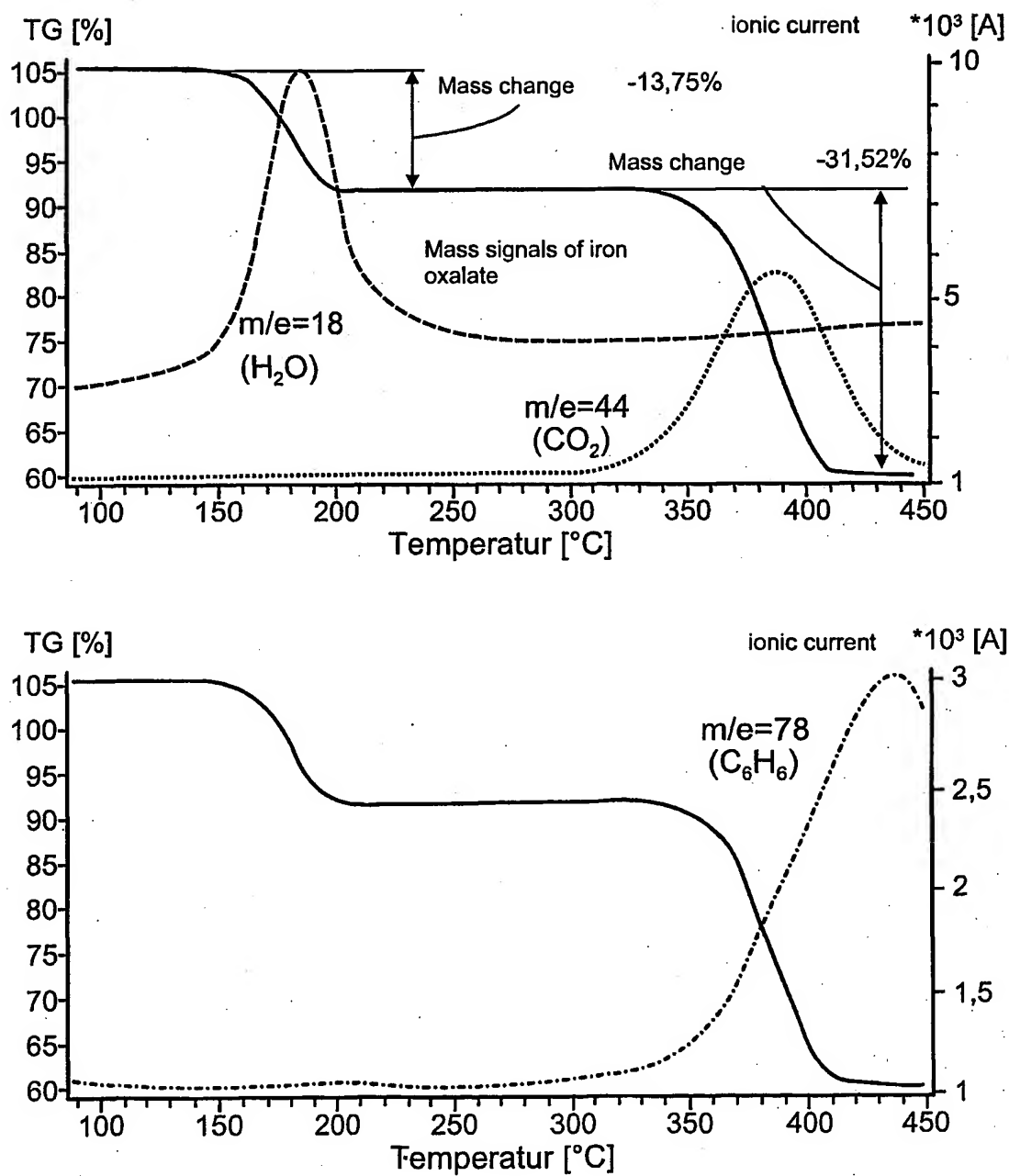


Fig.1

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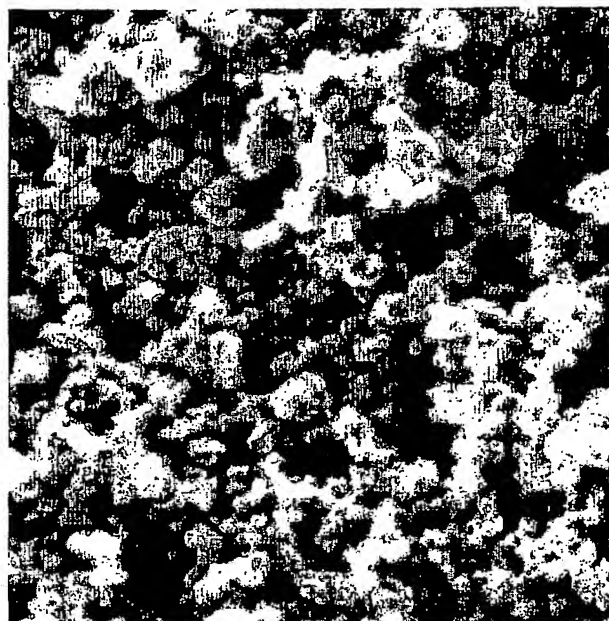
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Fig.2



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Fig.2

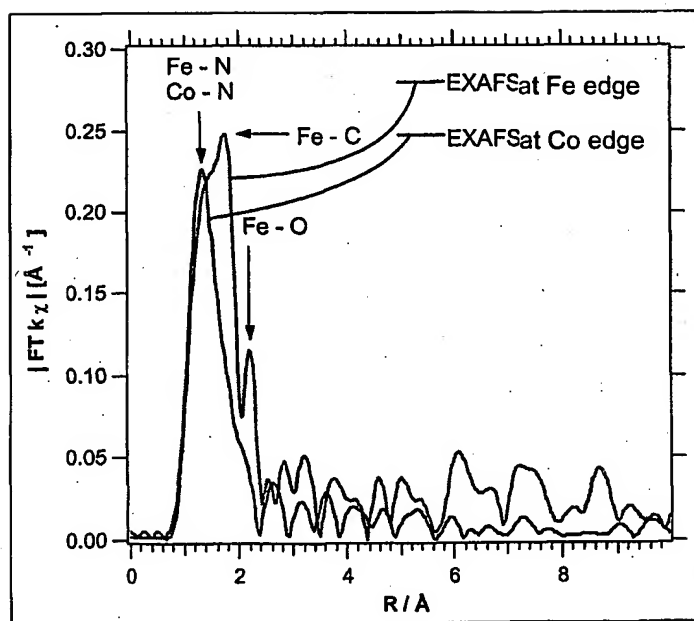


Fig.3

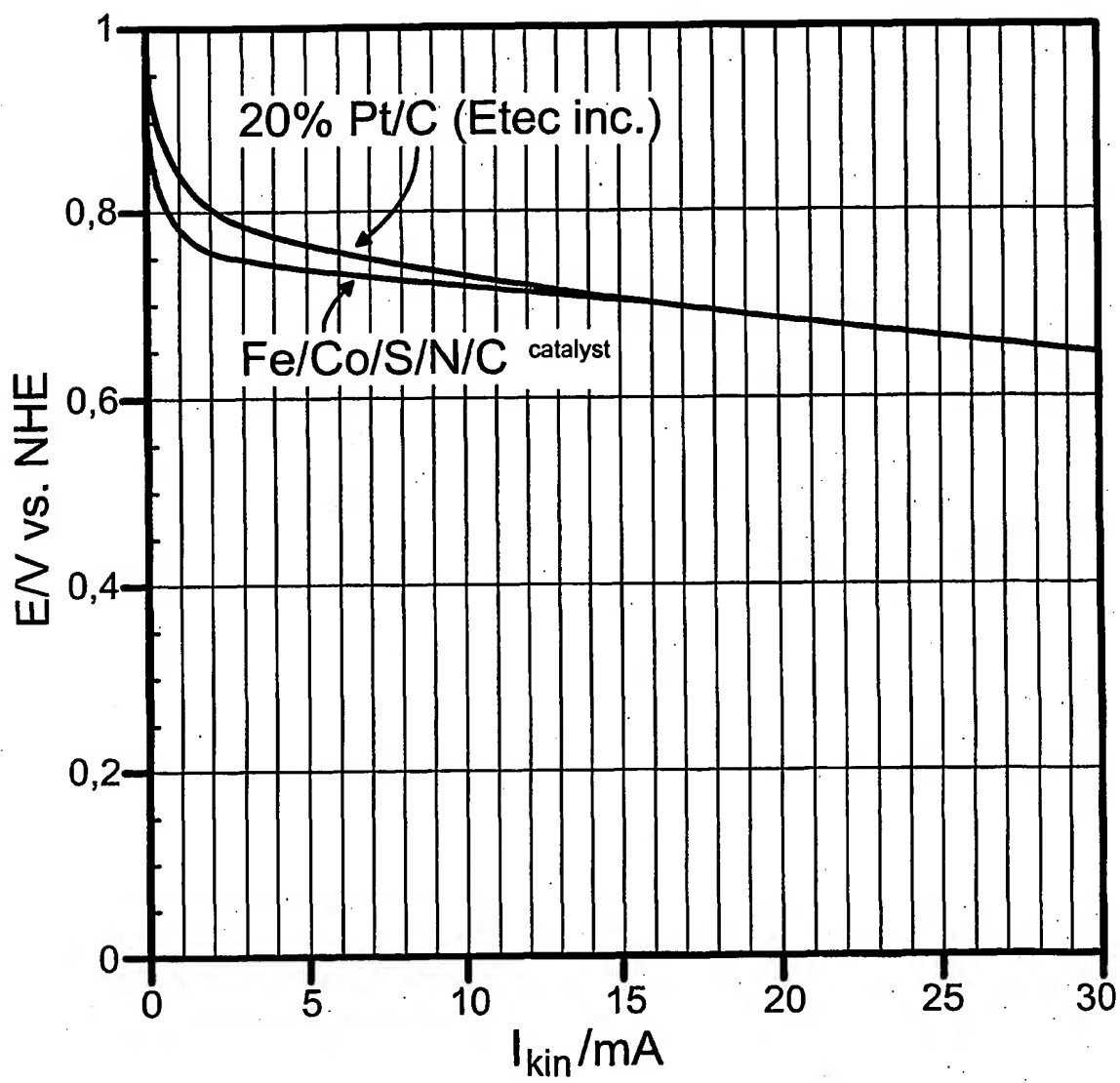


Fig.4

